JOURNAL OF CATALYSIS **147**, 177–185 (1994)

# The Conversion of Methanol and Other O-Compounds to Hydrocarbons over Zeolite $\beta$

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Received May 28, 1993; revised October 8, 1993

**The conversion of alcohols, ethers, and carbonyl compounds using zeolite $\beta$, zeolite ZSM-5, and zeolite Y are compared and contrasted. The proton form of zeolite $\beta$ is found to be as active as H-ZSM-5 for this reaction, whereas zeolite Y is much less active. Zeolite $\beta$ gives isobutane as the major product from methanol conversion under all reaction conditions tested, together with significant selectivities to $C_2$ and $C_3$ hydrocarbons. The conversions of ethanol and propanol over zeolite $\beta$ lead to the almost exclusive formation of the corresponding alkene via water elimination. This is in contrast to ZSM-5, and hence zeolite $\beta$ does not exhibit the rapid secondary conversion reactions typified by ZSM-5 for alcohol conversion reactions. The high selectivity to iso-$C_4$ hydrocarbons is also found for zeolite $\beta$ for the conversion of acetone and acetic acid. The results are discussed in terms of the possible mechanisms for the formation of iso-$C_4$ hydrocarbons in high selectivity for zeolite $\beta$.** © 1994 Academic Press, Inc.

## INTRODUCTION

Since the observation that zeolite H-ZSM-5 could dehydrate methanol to form hydrocarbons (1), highly siliceous zeolites have been investigated for a wide range of processes (2–4). However, it is clear that research has been dominated by the pentasil zeolite ZSM-5. It is interesting to note that zeolite $\beta$ was synthesised by Wadlinger *et al.* (5) as the first of a series of highly siliceous zeolites that were prepared in the research laboratories of Mobil Oil Corporation (6). At that time zeolite $\beta$ did not find commercial application, as its synthesis was overshadowed by the identification of the catalytic properties of the pentasil zeolites (1). Only in comparatively recent studies has zeolite $\beta$ received any attention when it has been reported as a catalyst for a number of conversion processes relevant to the production of fine chemicals (7, 8).

The structure of zeolite $\beta$ has been the subject of several studies. Early investigations (9, 10) suggested that zeolite $\beta$ comprised a 12-ring pore system, which was considered to be a channel structure rather than a cage structure, since Higgins *et al.* (11) found that the tetraethylammonium cation can be exchanged completely. For many preparations the X-ray diffraction pattern consists of a combination of broad and sharp reflections, from which it is considered that zeolite $\beta$ has an extensively faulted structure. Recently, Treacy and Newsam (12) have shown that zeolite $\beta$ is an intergrowth of two distinct but closely related 12-ring structures, both exhibiting three-dimensional pore systems. Hence, the structure of zeolite $\beta$ has features in common with both zeolite ZSM-5 (channel pore system, high Si/Al ratio) and zeolite Y (12-ring pore system), and these features may have important consequences with respect to the catalytic performance of zeolite $\beta$. The purpose of this study is to compare and contrast the catalytic performance of zeolite $\beta$ with H-ZSM-5 and zeolite Y for the conversion of O-containing compounds and thereby to investigate the relationship between structure and activity for these zeolites.

## EXPERIMENTAL

### *Zeolite Catalysts*

Zeolite $\beta$ was prepared according to the method of Wadlinger *et al.* (5). Sodium aluminate was prepared by dissolution of aluminium wire in aqueous sodium hydroxide and mixed well with aqueous tetraethylammonium (TEA) hydroxide to give solution **A**. Silica (Cabosil M-5, BDH) was thoroughly mixed with water to give a homogenised gel, denoted solution **B**. Solutions **A** and **B** were mixed to give a gel with composition

$$((TEA)_2O)_{2.5}(Na_2O)_{0.9}(Al_2O_3)_{1.0}(SiO_2)_{27.1}(H_2O_{332}),$$

which was aged at room temperature for 24 h prior to heating at 150°C in a 1-liter stainless steel autoclave with stirring (250 rpm). This ageing process was crucial, since preparations aged at higher temperatures or for different time periods resulted in poorly crystalline material being prepared from the gel. After crystallisation for 14 days, the zeolite was recovered, washed with distilled water,

0021-9517/94 $6.00

TABLE 1

Conversion of Methanol over Zeolite $\beta$

| Temperature (°C) | 370 | | | 370 | | | 400 | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| WHSV ($h^{-1}$)[a] | 1.6 | | | 0.8 | | | 0.8 | | | |
| Time-on-line (min) | 60 | 100 | 180 | 60 | 100 | 180 | 60 | 100 | 180 | 320 |
| Methanol conversion (%) | 97.8 | 89.9 | 64.2 | 100 | 100 | 96.9 | 100 | 100 | 100 | 67.1 |
| | Product selectivity (% by mass) | | | | | | | | | |
| Methane | 1.1 | 1.4 | 1.8 | 1.7 | 2.4 | 2.7 | 2.9 | 3.2 | 4.8 | 8.0 |
| $C_2$ | 15.4 | 16.5 | 17.2 | 16.9 | 19.2 | 19.4 | 19.6 | 20.2 | 22.2 | 20.8 |
| $C_3$ | 17.7 | 19.7 | 20.8 | 19.9 | 23.4 | 25.4 | 21.5 | 21.0 | 22.6 | 30.2 |
| Isobutane | 41.4 | 34.1 | 29.0 | 40.1 | 34.4 | 27.2 | 38.4 | 35.8 | 30.7 | 13.4 |
| 1-Butene | 0.8 | 2.0 | 2.9 | 0 | 0 | 2.0 | 0 | 0 | 1.4 | 4.4 |
| 2-Butene | 3.8 | 3.8 | 4.1 | 3.7 | 3.6 | 4.0 | 3.9 | 3.4 | 3.4 | 5.3 |
| $C_5$ | 14.0 | 14.8 | 15.2 | 11.7 | 11.5 | 12.1 | 9.5 | 11.3 | 10.3 | 10.1 |
| $C_{6+}$ | 6.1 | 7.6 | 8.8 | 5.9 | 5.3 | 7.1 | 4.1 | 5.0 | 4.3 | 7.6 |

[a] $N_2$ diluent: 30 ml $min^{-1}$.

dried at 120°C for 16 h, and calcined at 660°C for 16 h. The calcined zeolite was ion-exchanged with 0.1 *M* $NH_4NO_3$ (1 h, 100°C) and converted to the proton form (H-$\beta$) by calcination (660°C, 3 h). X-ray diffraction confirmed that the zeolite was H-$\beta$ and MAS NMR confirmed that only tetrahedral aluminium was present.

Zeolite ZSM-5 ($SiO_2/Al_2O_3$ = 30) was prepared according to the method of Howden (13) and exchanged with ammonium nitrate (0.1 M, 100°C, 1 h) dried and calcined (660°C, 3 h) to convert it to the proton form (H-ZSM-5) prior to use as a catalyst. Zeolite Y was purchased from Union Carbide.

### *Catalyst Evaluation*

Catalyst studies were carried out using a glass microreactor in which zeolite (0.5 g) was supported on silica wool. Reactants were fed to the reactor via a calibrated syringe pump and vaporised in a stream of dry nitrogen to give a controlled feedrate of reactant/$N_2$. Products were analysed by gas chromatography using three GC columns: 2 m Poropak Q temperature programmed from 50–200°C; 2 m Poropak T temperature programmed from 50–200°C; 30 m DB1 megabore column temperature programmed from 0–200°C. Product identification was supported by GCMS studies using a VG 7070 GC-MS fitted with an OV101 column.

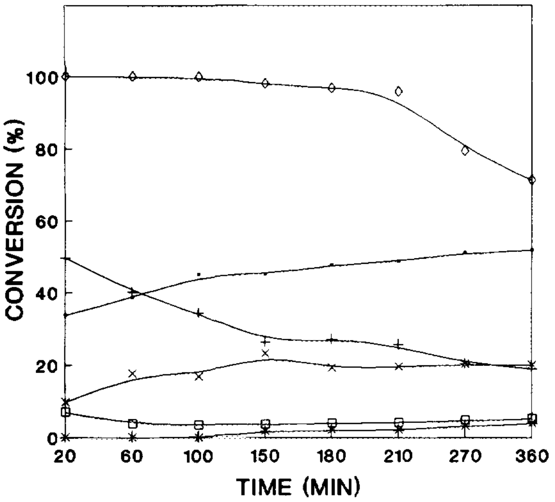

FIG. 1. Methanol conversion over zeolite $\beta$, 370°C, WHSV = 0.8 $h^{-1}$: effect of time-on-line. Key: (■) $C_1$–$C_3$; (+) isobutane; (*) isobutene; (□) butenes; (×) $C_{5+}$; (◇) methanol conversion.

## RESULTS

### *Methanol Conversion*

The conversion of methanol to hydrocarbons was investigated over zeolite $\beta$ and the results are given in Table 1. Zeolite $\beta$ displays high activity for this reaction and the products comprise mainly $C_2$–$C_4$ hydrocarbons with

TABLE 2

Methanol Conversion over Zeolites H-Y and H-ZSM-5 at 370°C and WHSV = 1.6 $h^{-1}$

| | H-Y | | | H-ZSM-5 | | |
|---|---|---|---|---|---|---|
| Time-on-stream (min) | 20 | 40 | 120 | 20 | 40 | 120 |
| Methanol conversion (%) | 78.4 | 73.5 | 54.0 | 97.8 | 94.3 | 93.8 |
| | Hydrocarbon selectivity (% by mass) | | | | | |
| Methane | 1.7 | 3.8 | 12.9 | 1.5 | 1.4 | 1.4 |
| Ethene | 21.7 | 21.2 | 24.6 | 24.1 | 20.9 | 20.6 |
| Ethane | 0.6 | 0.7 | 1.4 | 0.1 | 0.2 | 0.1 |
| Propene | 21.3 | 21.4 | 20.6 | 25.1 | 24.5 | 23.8 |
| Propane | 6.3 | 4.0 | 4.7 | 5.7 | 5.4 | 5.5 |
| Isobutane | 26.9 | 23.6 | 16.3 | 12.7 | 17.7 | 17.2 |
| 1-Butene | 2.5 | 3.9 | 5.3 | 2.3 | 2.1 | 2.3 |
| 2-Butene | 4.7 | 5.6 | 3.1 | 4.4 | 5.1 | 5.2 |
| $C_{5+}$ | 14.3 | 15.8 | 11.1 | 24.1 | 22.1 | 23.9 |

only small amounts of $C_{5+}$ hydrocarbons being formed. In particular, Zeolite $\beta$ displays high selectivity to isobutane (30–40%) under all reaction conditions investigated. The effect of time-on-line on conversion and selectivity is shown in Fig. 1. In general, conversion decreases with time-on-stream and the catalyst deactivates due to deposition of coke. For the experimental data given in Fig. 1, 0.05 g C was deposited on the catalyst during 370 min. For an analogous experiment at 400°C, 0.03 g C was deposited in the same time period, and in general coke was deposited at ca. 6–10% by mass of the catalyst depending on the temperature and WHSV for this length of experiment. As the catalyst deactivated, the selectivity to isobutane declined with concomitant increase in the selectivity to lighter hydrocarbons. This effect was most pronounced at low conversions.

The catalytic performance of zeolite Y and zeolite H-ZSM-5 ($SiO_2/Al_2O_3$ = 30, i.e., comparable to zeolite $\beta$) for methanol conversion under comparable conditions to that used for zeolite $\beta$ is shown in Table 2. It is apparent that the initial activity of zeolite $\beta$ is similar to that of zeolite H-ZSM-5 and is considerably greater than that of zeolite Y. However, zeolite $\beta$ deactivates more rapidly due to the enhanced rate of coking. It is clear that zeolite $\beta$ exhibits high selectivity to isobutane, a feature not exhibited by zeolite Y or zeolite H-ZSM-5.

### *Acetone Conversion*

The conversion of acetone to hydrocarbons over zeolite $\beta$ was investigated for a range of conditions and the results are given in Table 3. In addition, typical data showing the effect of time-on-line are shown in Fig. 2. Two striking features are immediately apparent. The first is that, at all

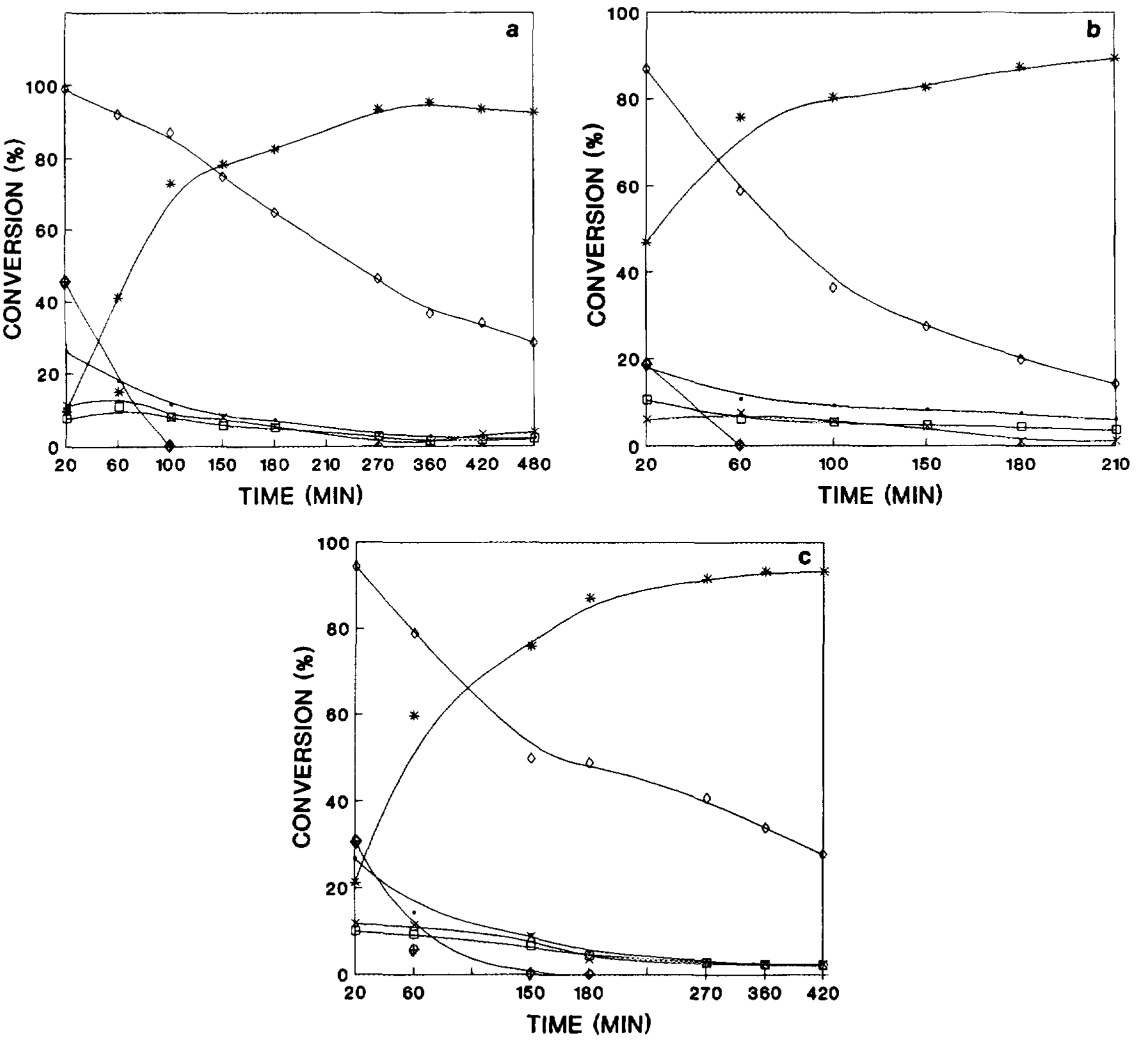

FIG. 2. Acetone conversion over zeolite $\beta$: effect of time-on-line: (a) 370°C, WHSV = 0.8 $h^{-1}$; (b) 370°C, WHSV = 1.6 $h^{-1}$; (c) 400°C, WHSV = 1.6 $h^{-1}$. Key: (▪) $C_1$–$C_3$; (◇) isobutane; (*) isobutene; (□) butenes; (×) $C_{5+}$; (◇) acetone conversion.

TABLE 3

Acetone Conversion over Zeolite $\beta$[a]

| Reaction temperature (°C) | 370 | 370 | 400 |
|---|---|---|---|
| Acetone WHSV ($h^{-1}$)[b] | 0.8 | 1.6 | 1.6 |
| Acetone conversion (%) | 64.6 | 37.1 | 48.8 |
| Product selectivity (% by mass) | | | |
| Methane | 0 | 0 | 0.1 |
| Ethane and ethene | 0.2 | 0.1 | 0.3 |
| Propane and propene | 7.1 | 2.5 | 4.7 |
| Isobutene | 82.3 | 93.0 | 87.1 |
| Isobutane | 0 | 0 | 0 |
| 2-Butene | 5.1 | 2.4 | 4.3 |
| $C_5$ | 2.6 | 1.9 | 3.2 |
| $C_{6+}$ | 2.7 | 0.1 | 0.3 |

[a] Data for time-on-line 180 min.

[b] $N_2$ diluent: 120 ml $min^{-1}$.

reaction conditions, zeolite $\beta$ has extremely high selectivity for total $C_4$ hydrocarbons (typically >90%). The second feature is that the major $C_4$ product is initially isobutane and as the catalyst deactivates due to coke deposition, the selectivity to isobutane is sharply decreased and the selectivity to isobutene dominates. Detailed GC and GCMS analysis was used to confirm the product assignments. Selectivities to isobutene in excess of 80% are readily achieved using zeolite $\beta$ as catalyst.

A comparison of the catalytic performance of zeolite $\beta$ and H-ZSM-5 ($SiO_2/Al_2O_3$ = 30) was also carried out (Table 4). H-ZSM-5 demonstrated lower overall selectivity to $C_4$ hydrocarbons, although isobutene was a major product within this fraction. As observed with zeolite $\beta$, isobutane selectivity is high during the initial reaction period and subsequently isobutene becomes the dominant $C_4$ hydrocarbon. It is apparent that zeolite H-ZSM-5 is considerably more active than zeolite $\beta$ for acetone conversion and so experiments were carried out at a lower temperature (Table 4). However, it was found that zeolite $\beta$ was always more selective than H-ZSM-5 for the formation of $C_4$ hydrocarbons, particularly isobutene, although at very low acetone conversions H-ZSM-5 can give high selectivities to isobutene, as noted previously by Chang and Silvestri (1).

TABLE 4

Acetone Conversion over Zeolite ZSM-5[a]

| Reaction temperature (°C) | 378 | 328 | 328 |
|---|---|---|---|
| Time-on-stream (min) | 120 | 100 | 360 |
| Acetone conversion (%) | 58.9 | 31.1 | 3.8 |
| Product selectivity (% by mass) | | | |
| $C_1 + C_2$ | 1.9 | 1.8 | 0.6 |
| Propane and propene | 11.7 | 6.4 | 1.1 |
| Isobutene | 25.7 | 51.2 | 78.8 |
| Isobutane | 0.6 | 0.3 | 0.1 |
| 1-Butene | 0.1 | 0 | 0 |
| 2-Butene | 7.9 | 4.9 | 1.3 |
| $C_5$ | 5.7 | 3.2 | 0.3 |
| $C_{6+}$ | 46.4 | 32.2 | 17.9 |

[a] WHSV = 1.6 $h^{-1}$

For zeolite $\beta$ an extended 7-h catalytic test was carried out at 370°C and acetone WHSV 1.6 $h^{-1}$. It was found that 0.05 g C was deposited as coke on the catalyst, which amounts to 1.6% C fed to the reactor. Under these conditions the major product was isobutene (selectivity ca. 90%), and in addition CO and $CO_2$ were formed at ca. 10% of the total yield of hydrocarbons. Similar levels of CO and $CO_2$ have been found in previous studies with H-ZSM-5 (1). The selectivity to CO and $CO_2$ shows interesting variations with increased reaction time, and representative data are shown in Fig. 3. It is apparent that during the initial reaction period when the selectivity to isobutane is high the selectivity to $CO_2$ is also high. Subsequently when isobutene becomes the significant product CO is formed almost exclusively. In addition the overall selectivity to carbon oxides remained unchanged throughout the reaction period and was consistent with 1 mol of carbon oxides being formed from 3 mol acetone converted.

Experiments were conducted for a range of acetone WHSV using zeolite $\beta$ at 370°C, and the plot of selectivity versus conversion is given in Fig. 4 for data collected at 180 min time-on-line. It is apparent that the high selectivity to isobutene is maintained across a very broad range of acetone conversions.

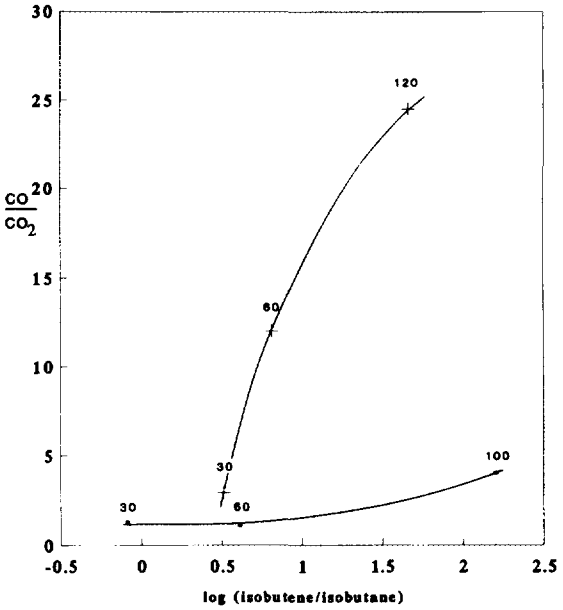

FIG. 3. Acetone conversion over H-ZSM-5 (WHSV = 1.6 $h^{-1}$): isobutene/isobutane ratio and $CO/CO_2$ ratio as a function of reaction time. Key: (■) 328°C; (+) 378°C; reaction times given in min.

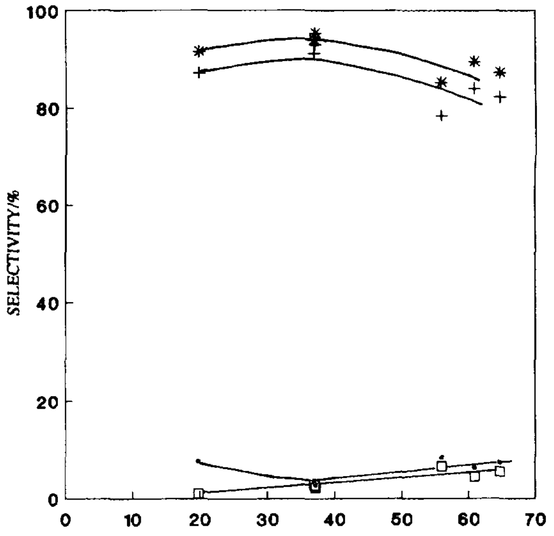

FIG. 4. Acetone conversion over zeolite $\beta$: selectivity versus conversion at 370°C, time-on-line 180 min. Key: (■) $C_1$–$C_3$; (+) isobutene; (*) total $C_4$; (□) $C_{5+}$.

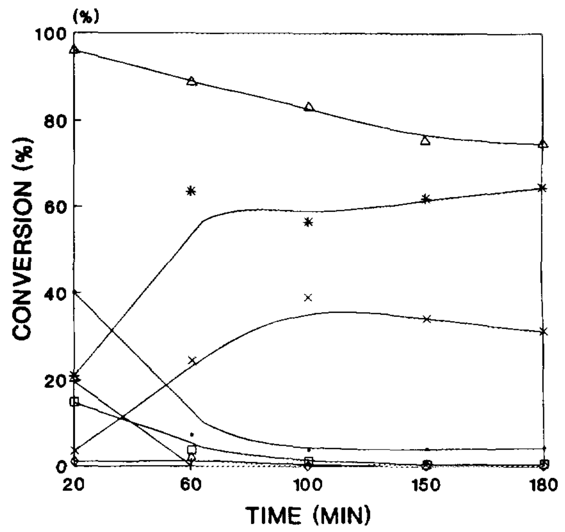

FIG. 5. Acetic acid conversion over zeolite $\beta$, 370°C, WHSV = 1.6 $h^{-1}$: effect of time-on-line. Key: (■) $C_1$–$C_3$; (+) isobutane; (*) isobutene; (□) butenes; (×) $C_{5+}$; (◇) acetone; (△) acetic acid conversion.

### *Conversion of $C_2$–$C_4$ Oxygen-Containing Compounds*

The conversion of a range of $C_2$–$C_4$ oxygen-containing compounds was investigated as reactants over zeolite $\beta$ and the results are given in Table 5. Ethanol, di-ethyl ether, 1-propanol, and 2-propanol were converted mainly to their corresponding alkenes, as would be expected for an acid-catalysed elimination mechanism. 2-Butanone gives a high selectivity to $C_5$ hydrocarbons probably in an analogous reaction to acetone conversion. Propanal was converted in high selectivity to aromatic hydrocarbons, as has previously been observed for H-ZSM-5 as catalyst. Interestingly, acetic acid conversion gave mainly isobutene and acetone as products, and data showing the effect of time-on-stream for acetic acid conversion are shown in Fig. 5.

## DISCUSSION

### *Alcohol and Ether Conversion*

Methanol conversion over zeolite $\beta$ gives mainly $C_2$–$C_4$ hydrocarbons as products over a wide range of reaction conditions with isobutane as the major product. Only a small fraction of the reaction products comprise $C_{5+}$ hydrocarbons. This is in contrast to the zeolite H-ZSM-5, where under comparable reaction conditions less isobutane and considerably more $C_{5+}$ hydrocarbons are formed. In addition zeolite $\beta$ and zeolite H-ZSM-5, which

TABLE 5

**Reaction of Oxygen-Containing Reactants over Zeolite $\beta$ at 370°C, WHSV 1.6 $h^{-1}$, Time-on-Line 100 min**

| | Ethanol | Diethyl ether | 1-Propanol | 2-Propanol | Propanal | Acetic acid | 2-Butanone |
|---|---|---|---|---|---|---|---|
| Conversion (%) | 100 | 100 | 100 | 100 | 30.9 | 83.2 | 26.4 |
| | | | Product selectivity (% by mass) | | | | |
| Methane | 0 | 0 | 0 | 0 | 0.2 | 0.8 | 0.1 |
| Ethene/ethane | 98.9 | 98.8 | 0.5 | 0.5 | 2.3 | 0.4 | 1.0 |
| Propene/propane | 0.5 | 0.5 | 84.6 | 83.2 | 19.1 | 2.4 | 5.2 |
| Isobutane | 0.3 | 0.2 | 2.2 | 3.6 | 0.9 | 0 | 1.3 |
| Isobutene | 0.1 | 0.1 | 3.0 | 0.7 | 5.3 | 56.5 | 7.1 |
| Butene | 0.1 | 0.1 | 4.7 | 5.2 | 7.5 | 1.0 | 10.0 |
| $C_{5+}$ | 0.1 | 0.3 | 5.0 | 6.8 | 64.7[a] | 0[b] | 75.3[c] |

[a] 59.6% benzene, toluene, xylene.

[b] 38.9% acetone.

[c] 49.0% $C_5$.

have similar $SiO_2/Al_2O_3$ ratios, exhibit comparable initial activities for this reaction, but zeolite $\beta$ deactivates more rapidly due to a higher level of coke formation. In comparison to zeolite Y, zeolite $\beta$ is considerably more active and exhibits a considerably longer catalyst lifetime. These differences in catalyst activity and selectivity are considered to be related to the micropore structure and $SiO_2/Al_2O_3$ ratios, i.e., number of Brønsted acid sites. As noted previously, the samples of zeolite $\beta$ and zeolite H-ZSM-5 used in this study have similar numbers of Brønsted acid sites and therefore the initial activities would be expected to be comparable. Furthermore, zeolite $\beta$ has a 12-ring pore system and would be expected to deactivate at a faster rate due to the deposition of coke, as is found for zeolite Y, which is also a 12-ring system. However, the difference in selectivity is not a manifestation of shape selectivity, since, on this basis, zeolite $\beta$ would be expected to give higher carbon number products than zeolite H-ZSM-5. The observation of lower carbon number products for zeolite $\beta$ indicates a lower reactivity of the active sites for secondary conversion reactions. This may be caused by the active centres being more remote from each other in zeolite $\beta$ due to the wider pore structure, or by the fact that methanol may not be able to cluster around these active centres, due to the pore geometry, as has been found for H-ZSM-5 by detailed infrared and NMR spectroscopy studies.

The lower reactivity of the Brønsted acid sites in zeolite $\beta$ is confirmed by the observations for the reaction of ethanol, propanol, 2-propanol, and dimethyl ether, which each form the corresponding alkene as the only significant product. This indicates that alkene oligmerisation is not a dominant reaction for zeolite $\beta$, which is in contrast to H-ZSM-5, which is very active for these reactions under comparable conditions (1, 14). In addition, under these conditions H-ZSM-5 is very active for hydrocarbon cracking and these reactions lead to the formation of ethene and propene (15). Hence the product distribution obtained from H-ZSM-5 is dominated by those of the secondary reactions. In contrast, it is therefore apparent that the products formed from methanol over zeolite $\beta$ reflect the composition of the initial product distribution for this reaction and that secondary conversion reactions are of limited importance for this reactant/zeolite system.

The rapid secondary conversion reactions have proved extremely problematical with respect to understanding the reaction mechanism of methanol conversion over zeolite H-ZSM-5 and therefore it is possible that zeolite $\beta$ may provide a better catalyst on which to study this reaction. It is interesting to note that the observation of isobutane as a principal product with lesser amounts of $C_2$ and $C_3$ hydrocarbons from methanol conversion is similar to the observation by Kolboe (16, 17), who found this product distribution from a DSC investigation of dimethyl ether adsorbed on H-ZSM-5. Recent mechanistic studies of methanol conversion have indicated that isobutane could be formed either via the sequential methylation of ethene and propene or via a concerted reaction between methanol and a surface alkoxy group (18–23), and both these pathways are schematically shown in Fig. 6. Since these routes can share common surface intermediates, it is not possible to differentiate between them at this stage (22, 23). However, only surface methoxyls have been shown to be present during the reaction (17–19), and to date there are no experimental data concerning the possible existence of surface ethoxy, isopropoxy, and t-butoxy intermediates. The scheme is therefore an indication of the possible pathways, and it is apparent that, in the absence of rapid secondary conversion of the initial $C_2$–$C_4$ hydrocarbon products, this reaction scheme can be used to rationalise the high selectivity for ethene, propene, and isobutane observed with zeolite $\beta$. Isobutane formation results from hydride donation to a 2-methylpropyl cation which is known to be a rapid reaction (24) and could occur either in the gas phase or on the surface.

### *Acetone Conversion*

Zeolite $\beta$ exhibits very high initial selectivity to isobutane and subsequently to isobutene following catalyst deactivation. It is considered that in the initial stages of the reaction, isobutane formation most probably results via hydride donation to a tertiary butyl cation, since this is known to be an exceptionally rapid process (24). Subsequently, proton loss from the tertiary butyl cation becomes dominant as the catalyst deactivates, leading to isobutene formation. The high selectivity to isobutene from acetone conversion is unusual and requires further comment. The catalytic self-condensation of acetone is known to be a complex reaction (25) leading to the formation of diacetone alcohol, mesityl oxide, phorone, mesitylene, isophorone, 3,5-xylenol, and 2,3,5-trimethylphenol as major products depending on the catalyst. For zeolite catalysts, Bosáček *et al.* (26) have carried out a detailed $^{13}C$ NMR spectroscopy study and have shown that, at low temperature, protonated acetone is formed which is subsequently transformed to diacetone alcohol. On heating to 180–280°C the NMR signals can be assigned to a complex range of products, in particular isophorone and alkylaromatics. It is therefore clear that a broad range of compounds will be formed from acetone over zeolite catalysts at elevated temperature and could therefore be active precursors for the formation of isobutene. Dolejsek *et al.* (27) have addressed the mechanism of formation of isobutene in high selectivity and have proposed a mechanism which involves the formation of mesityl oxide species and the decomposition of two molecules of mesityl oxide to give isobutene and $CO_2$ and $H_2O$ as products.

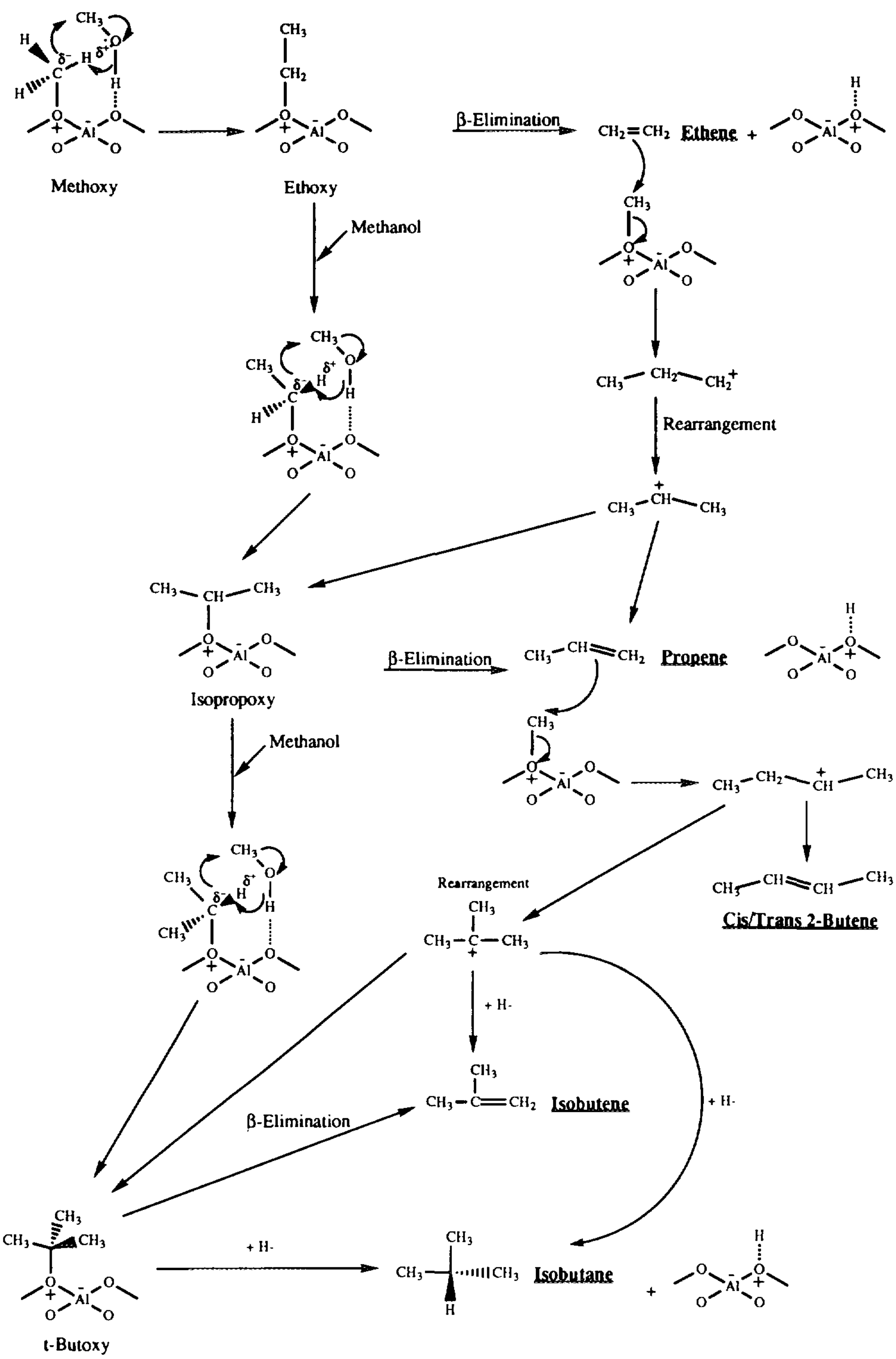

FIG. 6. Reaction of surface alkoxy groups on zeolite catalysts schematically showing the pathways possible for the formation of ethene, propene, isobutene, and isobutane.

However, although this mechanism explains the isobutene/CO ratio in the products on a stoichiometric basis, it is not clear how the two adsorbed mesityl oxide molecules interact to form the products. Decomposition of a single mesityl oxide molecule adsorbed on the zeolite would yield isobutene and a $C_2$ fragment, and this process would not be expected to give either the high isobutene selectivity or the isobutene/CO ratio observed.

It is therefore important to explore other possible precursor molecules for the formation of isobutene in high selectivity. It is noted (Fig. 2) that the selectivity to isobutene steadily increases with time-on-line, and it is possible that a surface species from the self-condensation of acetone is also formed at a corresponding rate. It is therefore necessary to consider the formation of isobutene from higher condensation products. Mesityl oxide can react with acetone at the terminal carbon $\alpha$ to the carbonyl group to form phorone which will cyclise to form isophorone. We consider that the high selectivity to isobutene could result from the acid-catalysed decomposition of phorone and isophorone (Fig. 7). Support for this proposal is provided by the NMR studies of Bosáček *et al.* (26), who observe phorone and isophorone as the products of self-condensation of acetone on zeolites. This mechanistic scheme also explains the observed isobutene/CO ratio observed in the products (1 mol carbon oxides from 3 mol acetone). The initial reaction of acetone over the zeolite results in the formation of isobutane and $CO_2$ and this would involve a different pathway. However, it is probable that both isobutane and isobutene could be formed from a number of intermediates formed from the acid-catalysed condensation of acetone depending on the precise reaction conditions.

A major difference between zeolites $\beta$ and ZSM-5 with respect to acetone conversion is that although both exhibit comparable catalytic activity, since this is related to the number of acid sites present, zeolite $\beta$ is considerably more selective for isobutene than is zeolite ZSM-5. This is considered to be due to the observation that zeolite $\beta$ is less active for the secondary conversion of alkenes, i.e., oligomerisation and cracking, that are dominant for zeolite ZSM-5, as has been discussed previously for methanol conversion.

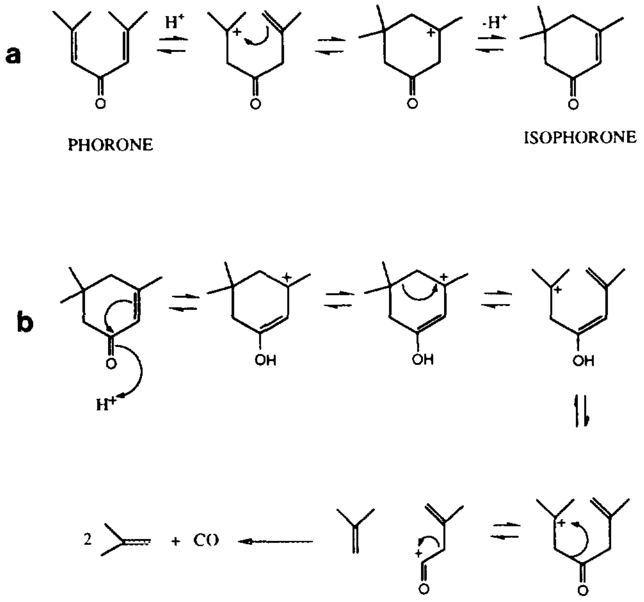

FIG. 7. Formation of isobutene by the acid-catalysed reaction of phorone and isophorone. (a) acid-catalysed interconversion of phorone and isophorone; (b) isobutene formation from isophorone.

### *Acetic Acid Conversion*

Acetic acid conversion over zeolite $\beta$ leads predominantly to the formation of acetone and isobutene in high selectivities. On the basis of the preceding discussion, it is likely that the isobutene results from the catalytic conversion of acetone. Hence, there is a catalytic route for the formation of acetone from acetic acid for zeolite $\beta$. Chang and Silvestri (1) also observed high selectivity to isobutene and a small amount of acetone for acetic acid conversion over H-ZSM-5 under comparable reaction conditions to those used in this study. Kuriacose and Swaminathan (28) showed that acetone could be formed selectively for the reaction of acetic acid over chromia and also by the thermal decomposition of chromium acetate. They considered that dehydration of acetic acid to give the acylium ion $CH_3\overset{+}{C}O$ which undergoes nucleophilic attack by acetate ion and elimination of $CO_2$ to form acetone. Chang and Silvestri (1) considered that this mechanism is also likely to occur for the zeolite ZSM-5. The model experiments using chromium acetate indicate that acetone arises from the reaction of two surface adsorbed acetate species, and this may be a general process for acid catalysts.

## CONCLUSION

Zeolite $\beta$ has been shown to be highly selective for the formation of iso-$C_4$ hydrocarbons from the conversion of methanol, acetone, and acetic acid. The high selectivity results in part from the observation that zeolite $\beta$ is less active for oligomerisation and cracking of hydrocarbons when compared with other zeolite catalysts. Methanol conversion is considered to occur either via a series of alkoxy intermediates or by sequential methylation of alkanes to form isobutane as the preferred product. The sustained high selectivity to isobutene from acetone and acetic acid is considered to result from the acid-catalysed decomposition of phorone and isophorone as the main reaction intermediates.

## ACKNOWLEDGMENTS

We thank the SERC Interfaces and Catalysis Initiative and the Industrial Affiliates of the Leverhulme Centre for Innovative Catalysis for financial support. Dr. D. Bethell is thanked for useful discussions.

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